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**1,7,8,9-Tetramethyl-2,3,5,6-tetrakis(trifluoromethyl)-4-thia-
10-oxatetracyclo[5,2,1,0^{2,6},0^{3,5}]dec-8-ene: A Diels–Alder Adduct from a Dewar-Type
Thiophene Derivative and a Furan Derivative**

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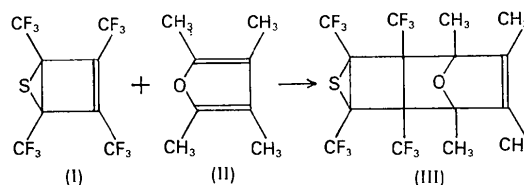
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Abstract. C₁₆H₁₂OF₁₂S, M.W. 480.1, monoclinic, *P*2₁/*a*, *Z*=4, *a*=14.351 (8), *b*=15.277 (8), *c*=8.409 (4) Å, β=98.96 (4)°, *U*=1821.1 Å³. *R*=0.138 for 2506 observed structure factors. It has been established that the Dewar thiophene part is linked to the furan ring with an *exo* configuration and that the thiirane ring involved in the Dewar thiophene part also takes an *exo* configuration with respect to the oxolane ring.

Introduction. In the course of a study of the reactivity of a Dewar-type thiophene which was recently synthesized by a photoisomerization reaction (Wiebe, Braslavsky & Hecklen, 1972; Kobayashi, Kumadaki, Ohsawa & Sekine, 1973), Kobayashi, Kumadaki, Ohsawa & Sekine (1974) obtained an adduct (III) by the Diels–Alder reaction of tetrakis(trifluoromethyl)-

5-thiabicyclo[2,1,0]pent-2-ene (I) with 2,3,4,5-tetra-methylfuran (II). The present X-ray study has been undertaken in order to determine the structure of this new adduct.



The crystals were grown from methanol solution as colourless transparent needles elongated along the *c* axis. The lattice constants were calculated from the setting angles of 15 reflexions on a Rigaku four-circle

Table 1. Atomic parameters and their standard deviations ($\times 10^4$)Temperature factors are of the form $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	-30 (2)	3063 (2)	767 (4)	49 (1)	81 (2)	232 (6)	5 (1)	-3 (2)	-15 (3)
C(2)	1170 (7)	3437 (7)	652 (12)	54 (6)	60 (6)	174 (18)	12 (5)	12 (8)	13 (8)
C(3)	1719 (7)	3612 (6)	2419 (12)	59 (6)	30 (4)	195 (18)	7 (4)	20 (8)	4 (7)
C(4)	1585 (7)	2597 (6)	2795 (12)	50 (5)	36 (4)	185 (17)	5 (4)	26 (8)	-2 (7)
C(5)	1080 (7)	2471 (7)	1020 (12)	63 (7)	50 (6)	187 (19)	3 (5)	25 (9)	-15 (8)
C(6)	1302 (10)	3879 (11)	-847 (15)	85 (9)	118 (11)	208 (24)	16 (8)	1 (12)	47 (13)
C(7)	1341 (8)	4348 (7)	3303 (14)	68 (7)	49 (6)	265 (24)	16 (5)	12 (10)	-29 (10)
C(8)	1068 (8)	2272 (8)	4100 (15)	64 (7)	73 (7)	266 (25)	6 (6)	52 (11)	41 (11)
C(9)	1121 (9)	1701 (9)	-58 (15)	77 (8)	94 (9)	234 (24)	1 (7)	10 (11)	-65 (12)
O(11)	3004 (4)	2813 (4)	1909 (8)	51 (4)	46 (3)	222 (13)	4 (3)	43 (6)	10 (6)
C(12)	2861 (7)	3665 (6)	2523 (14)	49 (6)	34 (5)	275 (23)	-1 (4)	30 (9)	5 (8)
C(13)	3236 (7)	3564 (7)	4322 (13)	43 (5)	45 (5)	260 (23)	2 (4)	21 (9)	-19 (9)
C(14)	3153 (7)	2733 (7)	4675 (13)	40 (5)	55 (6)	242 (21)	7 (4)	25 (8)	10 (9)
C(15)	2689 (7)	2282 (6)	3113 (12)	52 (6)	43 (5)	181 (18)	6 (4)	32 (8)	15 (7)
C(16)	3282 (9)	4391 (8)	1662 (18)	68 (8)	58 (7)	419 (36)	-10 (6)	37 (13)	60 (13)
C(17)	3701 (9)	4297 (9)	5389 (19)	62 (8)	66 (8)	422 (37)	-10 (6)	-27 (13)	-60 (14)
C(18)	3475 (8)	2250 (9)	6252 (15)	68 (8)	97 (9)	215 (23)	5 (7)	-9 (10)	36 (12)
C(19)	2905 (8)	1318 (7)	2947 (16)	57 (6)	33 (5)	390 (31)	10 (4)	24 (11)	3 (10)
F(1)	642 (7)	3703 (8)	-2053 (9)	144 (8)	183 (9)	226 (15)	-17 (7)	-11 (9)	51 (10)
F(2)	1369 (7)	4713 (5)	-700 (11)	146 (8)	71 (5)	469 (23)	2 (5)	5 (10)	89 (9)
F(3)	2094 (6)	3588 (6)	-1342 (10)	118 (6)	140 (7)	294 (17)	12 (5)	71 (8)	60 (9)
F(4)	435 (5)	4437 (6)	3067 (13)	65 (5)	134 (7)	686 (31)	41 (5)	-24 (9)	-171 (12)
F(5)	1661 (8)	5081 (5)	2961 (16)	223 (11)	39 (4)	882 (42)	6 (5)	206 (18)	-24 (10)
F(6)	1555 (6)	4308 (7)	4844 (10)	109 (6)	164 (8)	330 (18)	61 (6)	-10 (8)	-110 (10)
F(7)	1482 (6)	2091 (11)	5404 (10)	77 (5)	419 (19)	260 (17)	-49 (8)	10 (7)	180 (15)
F(8)	677 (9)	1489 (7)	3610 (14)	226 (12)	106 (7)	577 (30)	-61 (7)	209 (16)	3 (12)
F(9)	321 (6)	2703 (8)	4247 (12)	86 (5)	197 (10)	453 (23)	49 (6)	104 (9)	119 (12)
F(10)	1984 (5)	1622 (5)	-492 (9)	114 (6)	98 (5)	309 (16)	4 (4)	51 (8)	-70 (8)
F(11)	946 (6)	961 (5)	584 (12)	127 (7)	55 (4)	539 (25)	-19 (4)	62 (10)	-39 (8)
F(12)	556 (7)	1796 (7)	-1457 (10)	145 (8)	142 (8)	307 (18)	20 (6)	-50 (9)	-93 (10)

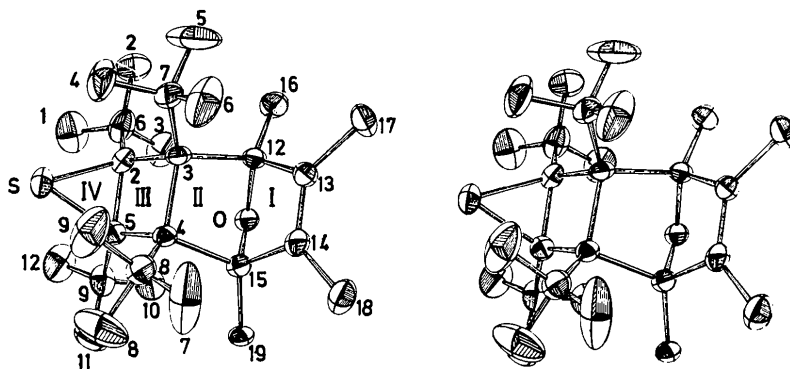


Fig. 1. A stereoscopic view of the molecule drawn by *ORTEP* (Johnson, 1965). The atoms are represented by ellipsoids of 10% probability.

diffractometer. Intensities were measured using graphite-monochromated $\text{Cu K}\alpha$ radiation by the θ - 2θ scan method with a scan speed of 4° min^{-1} in 2θ . The size of the crystal was about $0.2 \times 0.3 \times 0.5 \text{ mm}$. Of the total of 3423 reflexions within 2θ of 135° , 2506 had

structure amplitudes greater than $2\sigma(F)$ and were used for the structure determination. The observed data were corrected for Lorentz and polarization factors but no correction was applied for absorption. The normalized structure factors were then calculated using the scale and temperature factors determined by Wilson's method. The overall temperature factor was 5.6 \AA^2 . The structure was solved by the symbolic addition method (Karle & Karle, 1966) starting with three origin-specifying reflexions ($-10, 9, 2$; $10, 0, 1$; $3, 11, 6$) and five symbols. The E map calculated with 295 reflexions with E values greater than 1.7 gave all the non-

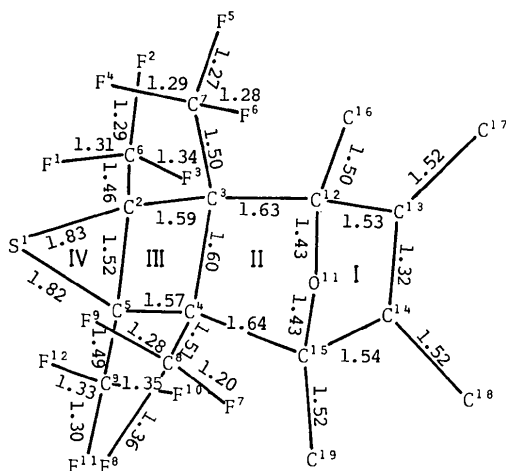


Fig. 2. Bond lengths (\AA).

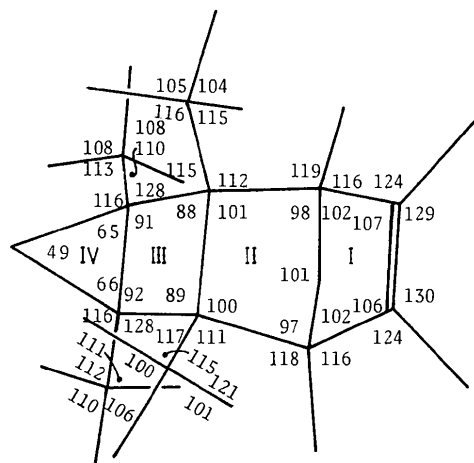


Fig. 3. Bond angles ($^\circ$). For angles not shown see Table 3.

Table 2. Planarity of the rings and interplanar angles between the rings

Equation of the plane is, $AX + BY + CZ = D$, where X , Y and Z are the orthogonal axes, $X||a^*$, $Y||b$ and $Z||c$, measured in \AA , and D (\AA) is the origin-to-plane distance.

Plane-forming atoms	Deviation	Atom	Deviation
I. 2,5-Dimethylfuran ring, $0.908X - 0.192Y - 0.371Z = 2.050$			
C(12)	0.01 \AA	O(11)	0.65 \AA
C(13)	-0.01	C(17)	0.08
C(14)	0.01	C(18)	0.10
C(15)	-0.01		
II. Oxolane ring, $0.073X + 0.227Y + 0.971Z = 3.018$			
C(3)	0.02	O(11)	-0.82
C(4)	-0.02		
C(12)	-0.01		
C(15)	0.01		
III. Cyclobutane ring, $0.875X - 0.191Y - 0.444Z = 0.332$			
C(2)	-0.01	S(1)	-1.56
C(3)	0.01		
C(4)	-0.01		
C(5)	0.01		
IV. Thiirane ring, $0.139X + 0.205Y + 0.969Z = 1.583$			
S(1)	0.00	C(3)	1.48
C(2)	0.00	C(4)	1.48
C(5)	0.00	C(6)	-1.09
		C(9)	-1.12

Interplanar angles

Between I and II	110°
II III	114
III IV	110

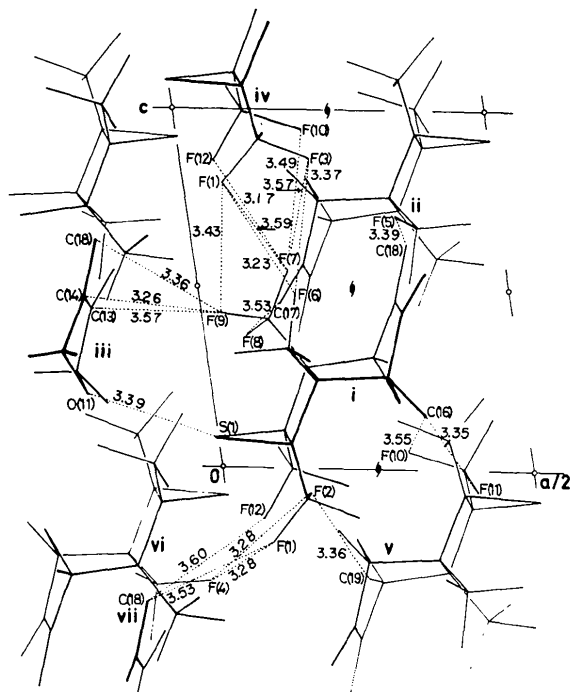


Fig. 4. Projection of the crystal structure along the b axis. Intermolecular interatomic distances less than 3.6 Å are shown. The equivalent positions are: i at x, y, z ; ii at $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$; iii at $-\frac{1}{2}+x, \frac{1}{2}-y, z$; iv at $x, y, 1+z$; v at $\frac{1}{2}-x, \frac{1}{2}+y, -z$; vi at $-x, 1-y, -z$; vii at $-\frac{1}{2}+x, \frac{1}{2}-y, -1+z$.

hydrogen atoms. Refinement was carried out by the block-diagonal least-squares method using the program *HBLS* (Okaya & Ashida, 1967), in which unit weight was attached for each observed reflexion. The R value could not be reduced below 0.138. This was probably because of large anisotropic thermal vibrations of fluorine atoms which may undergo rotational motions around the C–C bonds. The final atomic parameters are listed in Table 1.* The atomic scattering factors of C, O, F and S were those given in *International Tables for X-ray Crystallography* (1962) as SX-6, 8, 32a and SXC-69, respectively.

Discussion. Of several possible structures presumed for the adduct, the present analysis elucidated the one having the *exo* configuration of the cyclobutane ring with respect to the furan ring. The configuration of the thiirane ring was also confirmed as *exo* with respect to the oxolane ring.

A stereoscopic view of the molecule is shown in Fig. 1. The adduct molecule involves several planar groups. The planarity of each group and the dihedral angles between them are shown in Table 2. The bond lengths and angles are shown in Figs. 2, 3 and Table 3. The

Table 3. Bond angles ($^{\circ}$) not shown in Fig. 3

S(1)—C(2)—C(3)	110	C(4)—C(5)—S(1)	109
C(5)—C(2)—C(6)	130	C(2)—C(5)—C(9)	129
C(2)—C(3)—C(12)	114	C(2)—C(6)—F(2)	113
C(4)—C(3)—C(7)	124	F(1)—C(6)—F(3)	104
C(3)—C(12)—C(13)	104	C(3)—C(7)—F(5)	112
O(11)—C(12)—C(16)	114	F(4)—C(7)—F(6)	104
C(14)—C(15)—C(4)	107	C(4)—C(8)—F(8)	107
O(11)—C(15)—C(19)	113	C(7)—C(8)—F(9)	109
C(15)—C(4)—C(5)	114	C(5)—C(9)—F(11)	114
C(3)—C(4)—C(8)	124	F(10)—C(9)—F(12)	103

standard deviations are estimated to be 0.015 Å and 0.9° but larger values, 0.02 Å and 1.8° (or even greater if the bond-length contraction due to librational motions of the trifluoromethyl groups is taken into account), are expected for those involving fluorine atoms. As seen in Fig. 1, the molecule possesses approximate C_s symmetry. The bond lengths and angles clearly indicate the symmetry. The C–S–C angle of 49° in the thiirane ring is greatly distorted compared with that found in the free molecule of ethylene sulphide, 65.8°, obtained by a microwave spectroscopic study (Cunningham, Boyd, Myers, Gwinn & Le Van, 1951). The C–O–C angle of 101° is also significantly smaller than the values 108–113° which are commonly found in 2,5-dihydrofuran (110°; Beach, 1941) and other related compounds. The distortions of the bond angles may be caused by the ring formation: the cyclobutane ring for the C–S–C angle and the oxolane ring for the C–O–C angle.

The crystal structure is shown in Fig. 4. The molecules are packed together mainly by van der Waals forces between carbon and fluorine atoms (this type of interaction is predominant between the molecules i and ii, i and iii, i and v, and i and vii), between fluorine atoms (i and iv, i and vi) and between sulphur and oxygen atoms (i and iii).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30863 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.